Research Article

# Nanowire-Composite based Flexible Thermoelectric Nanogenerators and Self-Powered Temperature Sensors

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## ABSTRACT

We have developed a flexible thermoelectric nanogenerator (TENG) that is based on a Te-nanowire/poly(3-hexyl thiophene) (P3HT) polymer composite as the thermoelectric material with a positive Seebeck coefficient of 285 μV/K. A linear relationship between the output voltage of TENG and the temperature difference across the device was observed. Under a temperature difference of 55 K, two TENGs can provide an output voltage of 38 mV in serial connection, or a current density exceeding 32 nA/mm$^2$ in parallel connection. We demonstrated that the flexible TENG can be used as a wearable energy harvester by using human body temperature as the energy source. In addition, the TENG can also be used as a self-powered temperature sensor with a response time of 17 s and a reset time of 9 s. The detection sensitivity of the sensor can reach 0.15 K in ambient atmosphere.

## KEYWORDS

## 1. Introduction

Thermoelectric devices are based on the Seebeck effect that utilizes a temperature difference across the device to drive the diffusion of charge carriers [1]. They are very effective in harvesting electricity from waste heat with a temperature gradient relative to environmental temperature [2, 3], such as in cars, aircrafts, and power plants. Nanomaterials with higher performance are more attractive than their bulk counterparts for use in such thermoelectric devices since phonon scattering and energy-dependent scattering of electrical carriers occur in the presence of nanoscale interfaces [4–6]. Tellurium (Te) nanomaterials

have been demonstrated to have a high Seebeck coefficient of 408 μV/K [7]. Usually, the performance of a thermoelectric device is determined by the figure of merit ($ZT = \sigma S^2 T / \kappa$), where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $T$ is the average temperature, and $\kappa$ is the thermal conductivity [8]. Among these parameters, the most simple and direct way to design a device with excellent thermoelectric performance is to prepare a nanomaterial with high Seebeck coefficient. In addition, flexible devices have shown potential in wearable energy harvesting, space science, medical studies, and transportation [9]. Therefore it is to be expected that nanomaterial/polymer composites can provide the advantages of the high

Seebeck coefficient of the nanomaterial and the high electrical conductivity of the polymer, resulting in a device with high flexibility and performance [7, 10].

A self-powered sensing system drives sensors by harvesting energy from its working environment without batteries or other power sources [11–13]. By using the piezoelectric effect of nanomaterials [14–16], piezoelectric nanogenerators have been extensively applied in self-powered sensors [17, 18]. However, heat energy will be particularly important when the mechanical vibration is not available. The working mechanism of a thermoelectric nanogenerator (TENG) is based on the temperature difference across the device, suggesting that we can use the TENG's output as a self-powered temperature sensor that automatically detects the temperature difference across the device. In this work, we fabricated a TENG simply by mixing Te nanowires and P3HT polymer. The Te nanowires were synthesized at ambient temperature, which means that the energy-saving concept can be completely utilized, starting from the nanomaterial preparation. The as-prepared TENG showed a positive Seebeck coefficient of 285 μV/K and a linear relationship between the output voltage and the temperature difference across the device was observed. Under a temperature difference of 55 K, two TENGs can provide an output voltage of 38 mV in serial connection, or a current density exceeding 32 nA/mm$^2$ in parallel connection. We demonstrated that the flexible TENG can be used as a wearable energy harvester by using human body temperature as the energy source. In addition, the TENG can also be used as a self-powered temperature sensor with a response time of 17 s and a reset time of 9 s. The detection sensitivity of the sensor can reach 0.15 K.

## 2. Experimental

### 2.1 Growth of Te nanowires

Sodium dodecyl sulfate (SDS, $C_{12}H_{25}O_4SNa$, ≥ 99%) and hydrazine hydrate solution ($N_2H_4·H_2O$, 78%–82%) were purchased from Sigma–Aldrich. Tellurium dioxide ($TeO_2$, ≥ 99.9%) was obtained from Aldrich. Deionized water from a Milli-Q ultrapure (18.2 MΩ·cm) system was used in this study. Te nanowires were prepared

through the reduction of $TeO_2$ with hydrazine at ambient temperature. The $TeO_2$ was reduced to form Te colloids (amorphous and trigonal nanoparticles) and telluride ($Te^{2-}$) ions. The growth of Te nanowires was through the deposition of Te atoms (either oxidized from telluride ions or dissolved from amorphous Te nanoparticles) onto trigonal Te nanocrystallites. In a typical synthesis, hydrazine (50 mL) was added slowly to a beaker containing $TeO_2$ (0.5 g) at ambient temperature under constant magnetic stirring. The solution color changed from colorless to blue at the end of the reaction (180 min), indicating the formation of Te nanowires. The reaction was terminated by mixing the Te nanowires with 10 mmol/L sodium dodecyl sulfate solution (100 mL). The mixture was then subjected to three centrifugation/wash cycles to remove most of the matrices, including sodium dodecyl sulfate and hydrazine. Centrifugation was conducted at 6000 r/min and deionized water was used to wash the pellet (Te nanowires). The pellet was dried in air at ambient temperature prior to characterization and device fabrication.

### 2.2 Fabrication and measurement of the TENG and the self-powered temperature sensor

A composite of the Te nanowires and poly(3-hexyl thiophene) (P3HT) polymer in a mass ratio of 3:1 in $C_6H_5Cl$ solution was dropped onto a flexible substrate to produce a composite film. Silver electrodes were fabricated on the two ends of composite film structure, where the distance between two electrodes was about 6 mm. One end of the TENG was heated by a heater to produce the temperature difference across the TENG. A temperature sensor was used to record the temperature of the heater during all experiments. For the fabricated self-powered temperature sensor, one end of the sensor was attached on a thick glass substrate, serving as the sensitive unit. When the sensor was used to detect the temperature of exhalation, one end of the sensor was in contact with a heat sink module, which can keep this end at room temperature. The other end of the sensor was used as the sensing unit. The output performance of the device was measured by using a low-noise voltage preamplifier (Stanford Research System Model SR560) and a low-noise current preamplifier (Stanford Research

System Model SR570).

The mechanism of the TENG relies on the thermoelectric effect [1]. When forming a Te–P3HT composite, the Te nanowires are distributed randomly in the matrix, but certain portion of the nanowires are approximately parallel to the direction along the temperature gradient. These nanowires make the maximum contribution to the observed current. The P3HT serves as a conductive matrix for transporting the current and preserves the flexible entity of the entire device. The density of the Te nanowires in the matrix determines its thermoelectric performance.

## 3. Results and discussion

The fabricated TENGs are very flexible and can be attached on any substrate (such as Kapton film), as shown in Fig. 1(a) and Video 1 in the Electronic Supplementary Material (ESM). We also fabricated a composite of the Te nanowires and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) polymer (Video 2 in the ESM), which showed a clear fracture of the composite film under bending. This indicates that the P3HT is much better than PEDOT:PSS for fabricating flexible TENGs. As described in the Experimental section, the Te nanowires were grown at ambient temperature through a chemical reduction method. Figure 1(b) shows a Transmission Electron Microscopy (TEM) image of many Te nanowires, indicating that the length of the Te nanowires is about several micrometers. The TEM image and the corresponding High Resolution Transmission Electron Microscopy (HRTEM) image are shown in Figs. 1(c) and 1(d), respectively. The Te nanowires had a single crystalline structure with a diameter of about 12 nm.

Measurements made using the TENG are shown schematically in Fig. 2(a). A thin poly(dimethylsiloxane) (PDMS) layer was used to package the TENG to avoid any effects of the atmosphere. Two heaters with a distance of 6 mm were fixed on the two electrodes. The right heater was kept at room temperature and connected with the positive electrode of the measurement system. Figure 2(b) shows the cyclic change in temperature difference between the two heaters. The corresponding open-circuit voltage and short-circuit
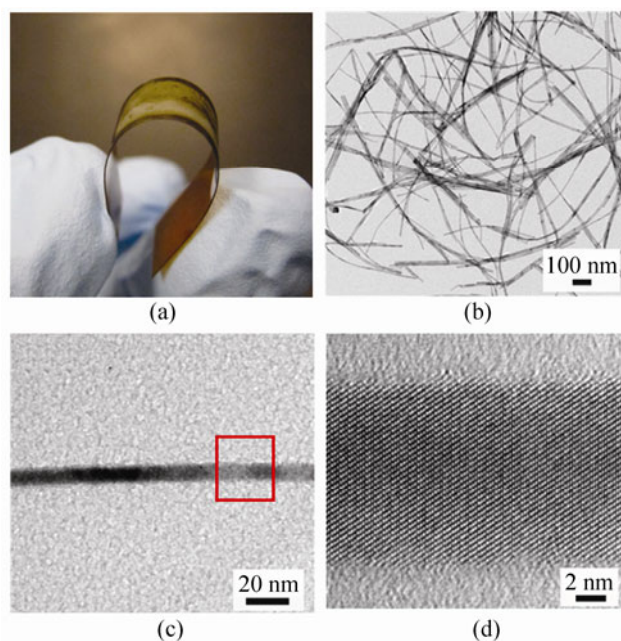


**Figure 1**  (a) Photograph of a Te-nanowire/P3HT-polymer composite device on a flexible Kapton substrate. (b) TEM image of Te nanowires. (c) TEM image of a single Te nanowire. (d) The corresponding HRTEM image of the Te nanowire in (c)

current of the TENG are shown in Figs. 2(c) and 2(d), respectively. Under forward connection, the output voltage/current (14 mV/254nA) was observed when the temperature difference was about 50 K (Fig. 2(c)). After reversing the connection of the TENG to the measurement system, the output voltage/current showed a corresponding opposite value (Fig. 2(d)), indicating that the measured signals were generated by the TENG. Figure 2(e) shows that the output voltage linearly increased with increasing temperature difference across the TENG. The calculated Seebeck coefficient is about 285 µV/K by using the equation $S = \Delta V/\Delta T$, where $\Delta V$ is thermoelectric voltage and $\Delta T$ is the temperature difference across the device [19]. The value is much larger than that of P3HT polymer (about 24 µV/K) but smaller than that of Te materials (about 408 µV/K) [7, 20].

To confirm that the total output of TENGs can be enhanced by integrating devices, a linear superposition test was carried out by using two TENGs in serial and parallel connection modes. Electrical measurement indicates that both TENGs exhibited Ohmic behavior with the Ag electrodes, as shown in Fig. 3(a). The total resistance of the TENGs was found to increase
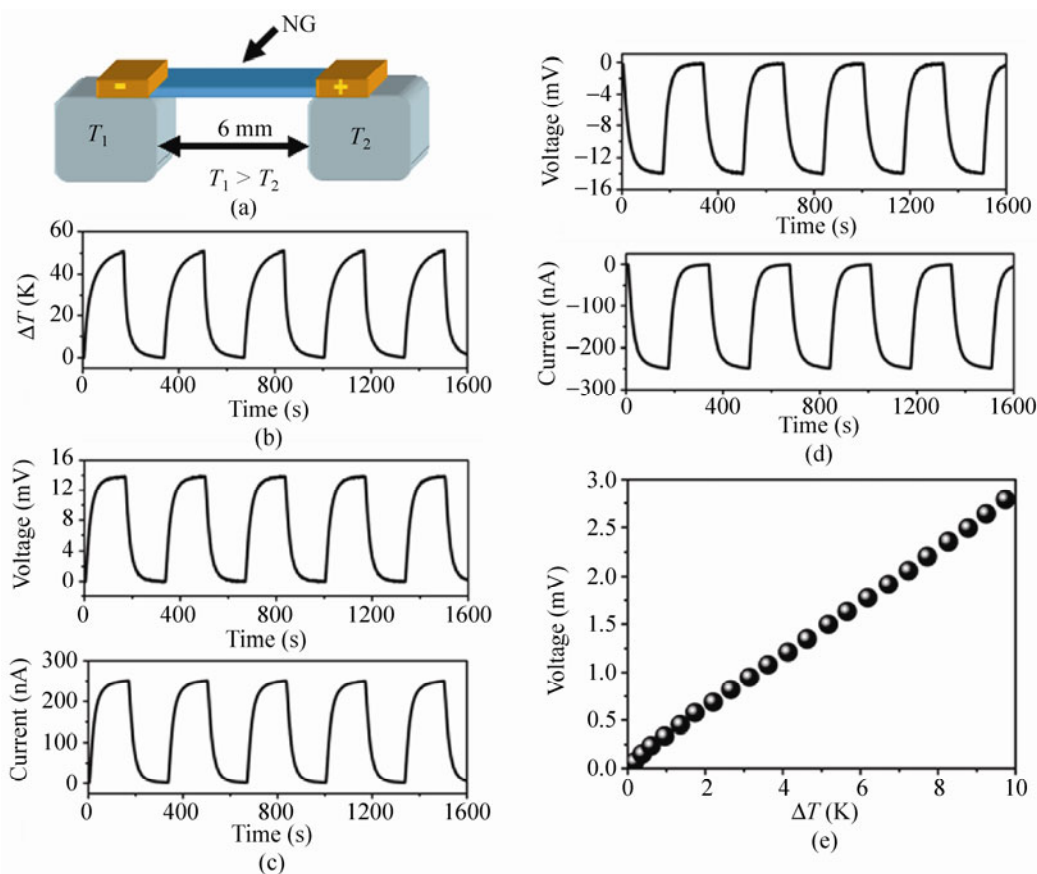
**Figure 2** (a) Schematic diagram of the measurements. (b) The cyclic change in temperature difference across the device. The output voltage and current of the TENG in forward connection (c) and reversed connection (d) to the measurement system. (e) The output voltage of the TENG as a function of change in temperature difference across the device

in serial connection mode, and decrease in parallel connection mode. Under a temperature difference of about 55 K (Fig. 3(b)), the output voltages of TENG1 and TENG2 reached 19 mV and 20 mV (Fig. 3(c)), respectively. The output current of TENG1 and TENG2 exceeded 120 nA and 201 nA (Fig. 3(d)), respectively. By integrating two TENGs in serial connection, the total output voltage reached 38 mV, as shown in Fig. 3(c). The total output current of TENG1 and TENG2 can exceed 320 nA (current density of about 32 nA/mm²), as shown in Fig. 3(d).

The TENG is flexible and can be fabricated on a Kapton substrate, as shown in Fig. 1(a). Figure 4(a) shows an optical image of a piece of fabric cloth, which has a white color. Figure 4(b) shows an optical image of the fabricated TENG after the Te-nanowire/ P3HT-polymer composite in $C_6H_5Cl$ solution was dropped onto the fabric in Fig. 1(a), after attaching the

fabric to a flexible Kapton substrate. The Ag film was coated on the fabric as the top electrode. The TENG was then attached on the human skin, as shown in Fig. 4(c). When there is a temperature difference between the skin and the surrounding environment, the output voltage/current of the TENG will be observed. The *I–V* characteristics of the TENG showed an Ohmic behavior, as shown in Fig. 4(d). Figure 4(e) shows that an output voltage of about 2.5 mV was observed when a cooler was in contact with the outer surface of the TENG. The corresponding output current was about 16 nA. When the cooler was moved out, the voltage/current recovered its original value. Although the output voltage/current of the TENG is much smaller than that in Figs. 2 and 3 due to the smaller temperature difference, these results indicate that the TENGs can be fabricated in the fabric cloth as a wearable energy harvester from human body.
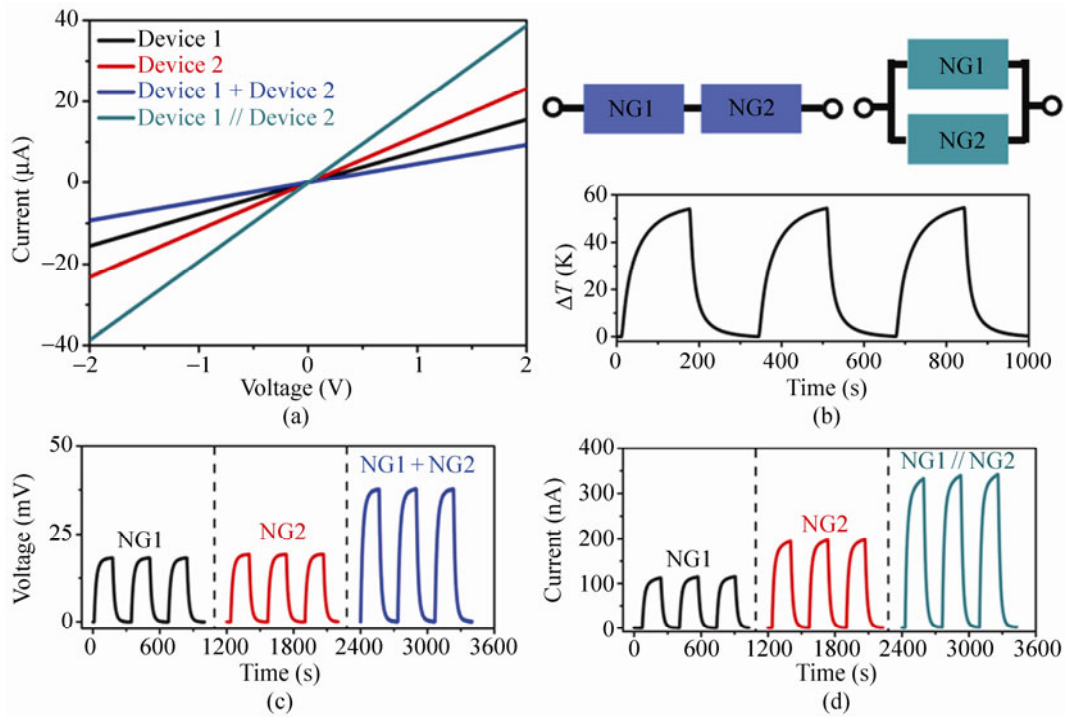
**Figure 3** (a) *I–V* characteristics of the device 1 and device 2. (b) The serial and parallel connection modes of the two devices and the change in temperature difference across the devices. (c) Electrical output voltage of the two devices in serial connection. (d) Electrical output current of the two devices in parallel connection
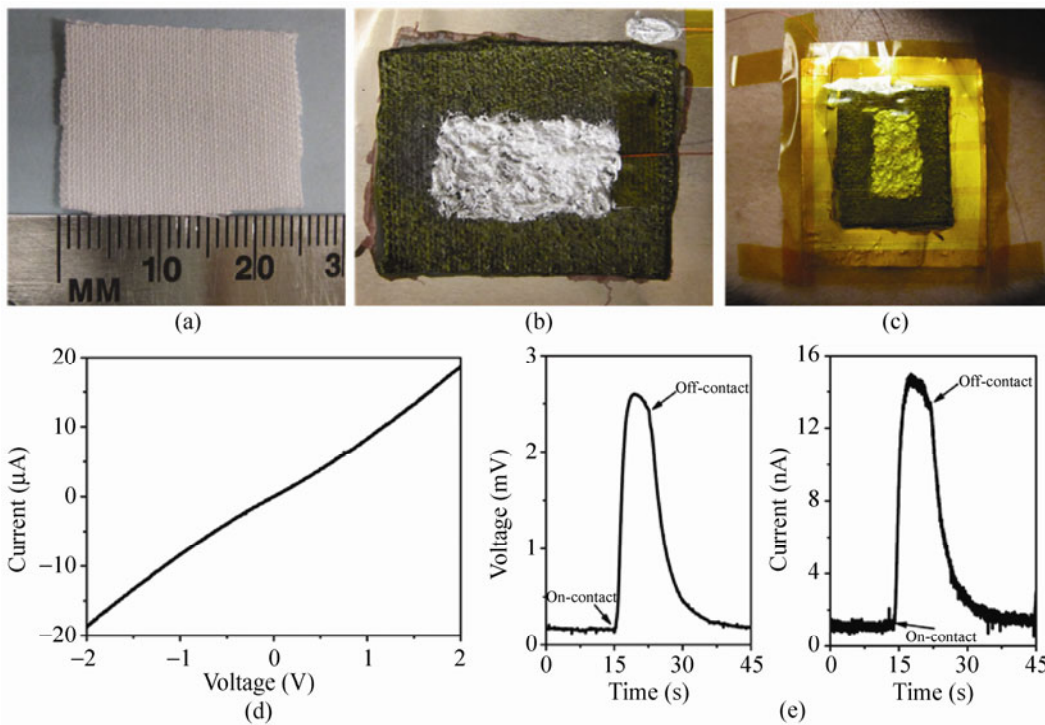


**Figure 4** (a) Photograph of a fixed-area fabric. (b) Photograph of the device fabricated onto a flexible Kapton substrate. (c) Photograph of the device attached on the human body. (d) *I–V* characteristics of the device. (e) Electrical output voltage and current when a cooler was contacted with the outer surface of the device

The behavior of the TENG is associated with both the Te nanowires and the P3HT polymer due to thermoelectric effect [7, 20]. According to the figure of merit ($ZT = \sigma S^2 T/\kappa$), the high Seebeck coefficient $S$ (408 μV/K) of Te nanowires can enhance the $ZT$ value of the composite device. Moreover, the good conductivity $\sigma$ of P3HT polymer can also result in a good $ZT$ value. In this study, we used Te nanowires since they have a high Seebeck coefficient and can be easily grown at ambient temperature through a simple chemical reduction method. There are two methods to improve the performance of the TENG further. One is to choose a nanomaterial with a higher Seebeck coefficient than that of the Te nanowires, which can further increase the $ZT$ value of the device. The other one is to use a polymer material with a higher conductivity than that of P3HT polymer. However, the polymer needs to be stable under cyclic mechanical deformation.

The fabricated TENG can be used as a self-powered temperature sensor, which can detect the temperature difference across the device. Figure 5(a) shows an optical image of the sensor, where the Te-nanowire/P3HT-polymer composite was attached on a thin glass substrate and the distance between two Ag electrodes was about 6 mm. One end of the sensor was fixed on a thick glass substrate, which was used as the detection end. When the sensor was in contact with a heat source (temperature of 298 K), the output voltage of the sensor under the forward/reversed connection is about 0.8 mV. The corresponding response time of the sensor was 17 s, as shown in Fig. 5(b). When the sensor was moved out, the output voltage returned to zero. The decay time of the sensor followed a second-order exponential decay function, as shown by fitting the $V$–$T$ curve in Fig. 5(c). The reset time of the sensor was about 9 s, which is defined as the time recovered to 37% of the original value. Figure 5(d) shows that the detection sensitivity of the sensor was about 0.15 K at room temperature, resulting in an output voltage
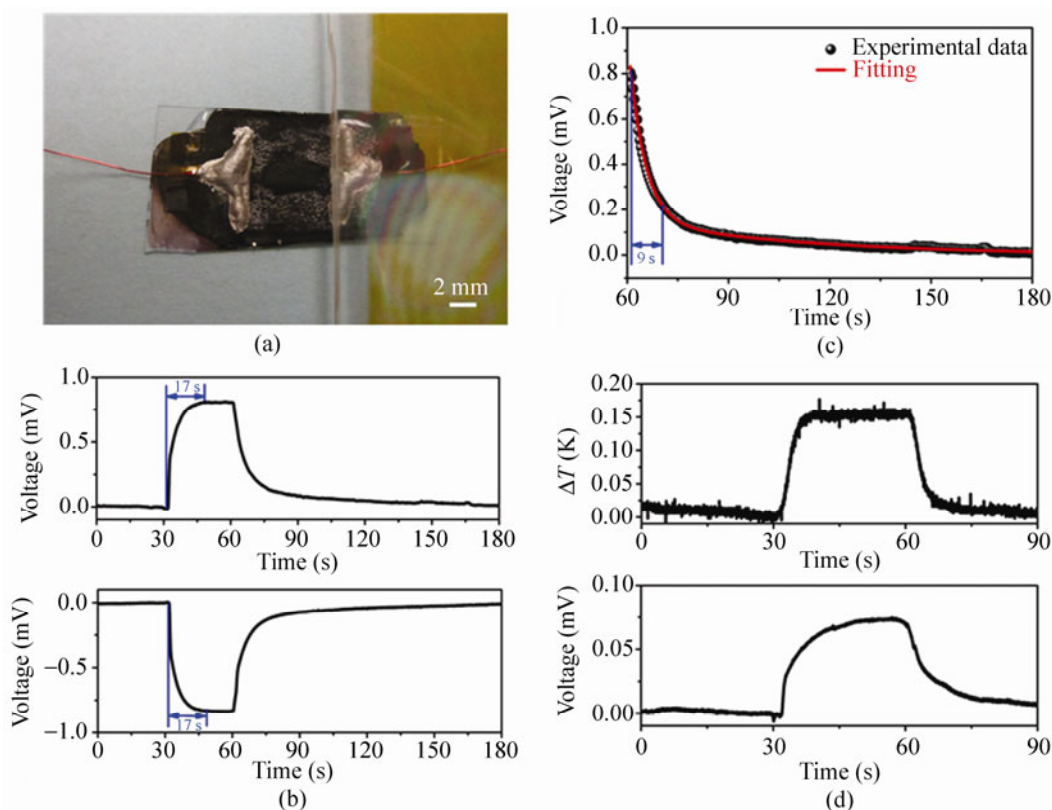


**Figure 5** (a) Photograph of the self-powered temperature sensor. (b) Electrical output voltage of the device when it was contacted with a heat source at a temperature of 298 K in forward connection and reversed connection conditions. (c) The $V$–$T$ curve when the sensor was moved out, showing that the reset time is about 9 s. (d) The change in small temperature difference across the device and the corresponding output voltage

of about 0.08 mV. Moreover, the linear relationship between the output voltage and the temperature difference across the device indicates that the sensors have a good performance near room temperature.

We also demonstrated that the self-powered sensor can be used to detect the temperature of the exhaled air from a human lung. Figure 6(a) shows the measurement system, where the sensor in Fig. 5(a) was attached on a wooden body. One end of the sensor is in contact with a heat sink module, which can keep this end at room temperature. The other end of the sensor was used as sensing unit. When the air that can be expired after maximal inspiration was in contact with the sensitive unit of sensor, the temperature difference between two ends of the sensor will produce an output of voltage. Figure 5(b) shows that the output voltage peak of the sensor is about 1.4 mV. The corresponding measurement process is recorded in Video 3 (in the ESM). According to the results in Fig. 2(e) for a room temperature of about 295 K, the measured temperature peak of the air in the lung is about 300 K.
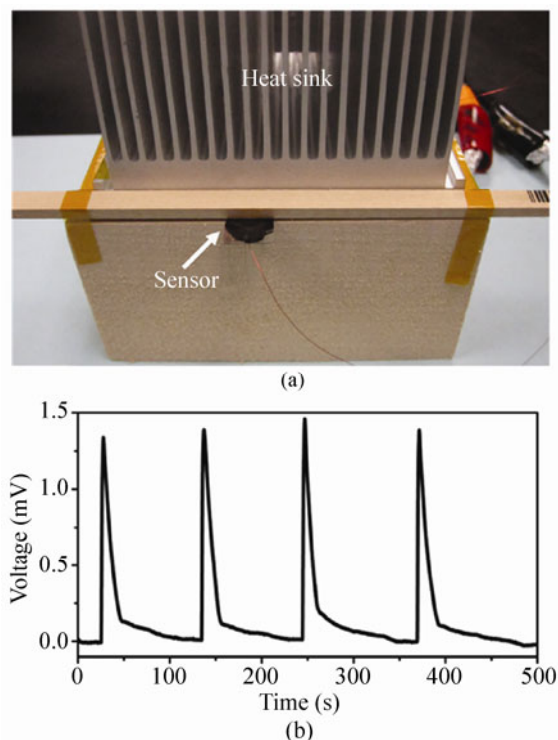


**Figure 6** (a) Photograph of the noncontact temperature measurement system. (b) Electrical output voltage when the air that can be expired after maximal inspiration was in contact with the sensitive unit of the sensor for four times

## 4. Conclusions

We have demonstrated a flexible thermoelectric nano-generator based on a Te nanowire/P3HT polymer composite, which has a positive Seebeck coefficient of about 285 µV/K. The output voltage of the device was found to linearly increase with increasing temperature across the device near room temperature. The flexible device can be used as a wearable energy harvester. The self-powered temperature sensor has a response time of about 17 s and a reset time of about 9 s. The temperature of the exhaled air in lungs was measured to be about 300 K by using this sensor. This study demonstrates the possibility of using a Te nanowire/P3HT polymer composite for wearable thermoelectric energy harvesting and self-powered temperature sensors.

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